# Thermodynamics of thermoresponsive polymer PNIPAM in aqueous solutions

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> 1st Users Conference of IT4I Tuesday, October 31, 2017













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pNIPAM thermodynamics

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#### Outline









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#### Smart Materials based on thermoresponsive polymers



Stuart et al. Nature Materials, 2010, 9, pp. 101-113

- Large changes in a material property upon a application of a small external stimuli
  - Temperature, pressure, stress, moisture, light
  - Change of pH, addition of salt
- This change is revesible and controlable
  - Volume phase transition
  - Conformation (cis/trans)
  - Polarity
  - Optical properties (transparent/opaque)
  - Electrical properties ((non-)conductive)
- Near transition sensitive to another stimuli
  - $\bullet \ \rightarrow \text{Multiresponsive materials}$



- System:
  - 1 PNIPAM chain in 6nm cubic box filled with 10k water molecules
  - Different force-fields employed and fine-tuned
  - Different chain lengths investigated
- Method and scalability:
  - Direct MD hopeless for thermodynamics
  - Replica Exchange MD (REMD) technique for sampling
  - 76 replicas spanning the temperature range 270-420 K
  - Equilibration  $\approx$ 50-100 ns, production  $\approx$ 100 ns per replica
  - Gromacs 5.1.2 package was used
  - $\bullet\,$  Large number of particles  $\rightarrow$  good scaling
  - 1 replica per 1 core  ${\approx}5\,\text{ns/day},$  1 replica per node (24 cores) provides  ${\approx}85\,\text{ns/day}$
  - $\rightarrow$  **76x24=1824** cores/job (Salomon cluster)
- Analysis:
  - Coil  $\leftrightarrows$  Globule equilibrium sampled  $K = P_{coil}/P_{globule}$
  - Direct access to transition free energy,  $\Delta G = -RT \ln K$



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#### Enhanced sampling via replica exchange MD simulation



- Independent short MD runs in parallel at a set of temperatures
- Frequent Monte-Carlo-like swap moves between neighbors
- Largely increased sampling of the conformational space at all Temp.
- Very suitable for thermodynamic studies (all Temp. in a single run)

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Zacharias et al., J. Phys.: Condensed Matter, 2015, 27, pp. 323101



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#### Theory: Meeting atomistic and macroscopic properties



Algaer et al. *JPCB*, 2011, 115, pp. 13781 Heyda et al. *Macromolecules*, 2013, 46, pp. 1231 Heyda et al. *JPCB*, 2014, 118, pp. 10979 Okur et al. *JPCB*, 2017, 121, pp. 1997

$$K = \frac{P_{coil}}{P_{globule}} \rightarrow \Delta G = -RT \ln K$$
$$\left(\frac{\partial \Delta G}{\partial T}\right) = -\Delta S \quad \left(\frac{\partial \Delta G}{\partial c_3}\right) = -RT \Delta \Gamma_{23}$$
$$\Gamma_{23} = \rho_3 (G_{23} - G_{21}) \approx -\left(\frac{\partial \mu_2}{\partial \mu_3}\right)_{p,T,m_2} \quad \text{(dialysis exp.)}$$
$$\Delta G(\Delta T, c_3) \simeq \Delta G(T_0) + \frac{\partial \Delta G}{\partial T} \Big|_0 \Delta T + \frac{\partial \Delta G}{\partial c_3} \Big|_0 c_3 + \dots \quad \text{(Taylor)}$$
$$\Delta T(c_3) = -\frac{RT \Delta \Gamma(c_3)}{\Delta S_0 + RT \left(\frac{\partial \Delta \Gamma}{\partial T}\right) c_3} \quad \text{(all together)}$$

#### 1-water, 2-PNIPAM, 3-salt

 $G_{21}, G_{23}$  – Kirkwood-Buff integrals (effective exluded volume)  $\Gamma_{23}$  – Preferential interaction (excess number of particles)

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● Depleted salt affects △T pNIPAM thermodynamics

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Image: A math the second se

• Depleted salt affects  $\Delta T$ 

pNIPAM thermodynamics



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pNIPAM thermodynamics



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Polak, J.; Palivec, V.; Kovalcik, A.; Ondo, D.; Heyda, J. in preparation



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- coil  $\rightleftharpoons$  globule equilibrium  $\Rightarrow \Delta G_U(T) = -RT \ln \frac{[C_{oil}](T)}{[G_{lobule}](T)}$

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• These two stimuli ( $c_{salt}$  and  $\Delta T$ ) compensate at new LCST



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## Hard experimental thermodynamic data



- Excluded salts cause linear decrease of LCST, i.e., cloud-point, (NaCl, Na<sub>2</sub>SO<sub>4</sub>)
- Salts with excess on polymer surface lead to weak nonlinear increase (NaSCN)
- Polak, J.; Palivec, V.; Kovalcik, A.; Ondo, D.; Heyda, J. in preparation

- Excluded salts have no or marginal effect on transition enthalpy (NaCl, Na<sub>2</sub>SO<sub>4</sub>)
- Enriched salts significantly decrease the transition enthalpy (NaSCN)



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#### Conclusion

- Highly paralelized REMD was employed to:
  - develop reliable force-field of pNIPAM
  - investigate thermodynamic properties in water
  - investigate effect of salt on thermodynamics
  - quantify salt excess and/or depletion
- Results are complemented with experiments:
  - cloud-point measurements
  - DSC calorimetry
  - ITC calorimetry
- Outlook:
  - effect of the polymer chain length on LCST
  - role of finite polymer concentration (i.e., many chains)





#### Acknowledgement

- Experiments: Jakub Polak, Adam Kovalcik, Daniel Ondo (LCST, ITC, DSC)
- Simulations: Vladimir Palivec, Denis Zadrazil, Emil Pavelka- see our poster



- Czech Science Foundation, Grant 16-57654Y
- CIISB proposal at CEITEC-MU Brno (DSC, DLS, SAXS)
- IT4Innovations National Supercomputing Center LM2015070
  - Project OPEN-7-50
  - Project OPEN-10-36

## Thank you for your attention



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- monthly salary of 3.000 EUR + consumables
- support of excellent mentors
- possibility of establishing your own independent research group
- position available as of 1 April, May or June 2018

Submit your application via e-mail to <u>marika.kurova@vscht.cz</u> before Monday 27<sup>th</sup> of November 2017, 23:59 Brussels time.



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IT4I, 31.10. 14 / 15

#### Theory: Meeting atomistic and macroscopic properties



Algaer et al. *JPCB*, 2011, 115, pp. 13781 Heyda et al. *Macromolecules*, 2013, 46, pp. 1231 Heyda et al. *JPCB*, 2014, 118, pp. 10979

Okur et al. JPCB, 2017, 121, pp. 1997

$$\Delta G(\Delta T, c_3) \simeq \Delta G(T_0) + \frac{\partial \Delta G}{\partial T} \Big|_0 \Delta T + \frac{\partial \Delta G}{\partial c_3} \Big|_0 c_3 + \dots \text{ (Taylor)}$$

$$\Gamma_{23} = \rho_3 (G_{23} - G_{21}) \approx - \left(\frac{\partial \mu_2}{\partial \mu_3}\right)_{p,T,m_2}$$

$$\Delta \Gamma_{23} = \Gamma_{c3} - \Gamma_{g3} \rightarrow \mu_c - \mu_g = \Delta G(c_3) \text{ ... Gibbs E.}$$

$$\Delta \Gamma(c_3, \Delta T) = \Delta \Gamma' c_3 + \frac{1}{2} \Delta \Gamma'' c_3^2$$

$$\Delta T(c_3) = -\frac{\Delta \Gamma' c_3 + \frac{1}{2} \Delta \Gamma'' c_3^2}{\frac{\Delta S_0}{k_B T_0} + \left(\frac{\Delta \Gamma'}{T_0} + \frac{\partial \Delta \Gamma'}{\partial T}\right) c_3}$$

• 1-water, 2-PNIPAM, 3-salt  $G_{21}, G_{23}$  – Kirkwood-Buff integrals (*effective exluded volume*)  $\Gamma_{23}$  – Preferential interaction (*number of particles*)

Image: A mathematical states of the state

- Depleted salt affects  $\Delta T$
- Binding salt affects  $\Delta T$  and  $\Delta H$



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